Enhancement of Gas Sensing Properties of SnO2 Nanoparticle Thick Films by Loading Pd, Pt and Pd-Pt Catalysts at Low Temperatures

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論　文　内　容　要　旨

In this thesis, gas sensing properties of tin oxide nanoparticle thick film such as sensitivity (R_{3500}/R_{1000}), response and recovery time were enhanced to 0.58, less than 0.4 and 1 minute by newly developed low temperature catalyst loading method. The low temperature catalyst loading method is to load the catalysts onto the surface of tin oxide nanoparticle under low temperature of 300°C instead of 700°C, which is required to burn out the Cl and NO_3 that are contained in conventional method. So, the lowering of the temperature could be achieved by excluding the harmful elements. Also, by lowering the temperature of catalyst loading, suppression of particle growth of the tin oxide nanoparticle could be realized. Then, in order to enhance the gas sensing properties, optimal condition of catalytic factors like catalyst materials, catalytic configuration, and loading step was investigated.

In chapter 1, background and purpose of this thesis were introduced. The particle growth problem of tin oxide nanoparticles by conventional high temperature catalyst loading process above 600°C was pointed out. Also, in order to solve the problem, low temperature catalyst loading method to suppress the particle growth with the low temperature of 300°C was newly proposed.

In chapter 2, experimental methods were explained. Synthesis of tin oxide nanoparticle, low temperature catalyst loading, in-situ synthesis and loading, fabrication of gas sensitive thick film, and characterization of tin oxide nanoparticle and gas sensitive thick film were explained.

From chapter 3 to chapter 7, experimental results were presented and discussed.

In chapter 3, Pd catalyst was loaded onto tin oxide nanoparticles, and gas sensitive thick film was fabricated.

Because the loading was carried out at the low temperature of 300°C, the growths of nanoparticles were successfully suppressed. Accordingly, 5 nm sized tin oxide nanoparticle loaded with Pd catalyst could be fabricated as shown in Fig. A-1. Even after heat-treatment at 600°C for fabrication of gas sensitive thick film, the particle growth could be successfully suppressed. It is attributed that the catalytic additives loaded onto surface of the tin oxide nanoparticle suppressed migration of the surface of the nanoparticle through the additive effects on interface migration. The gas sensitive thick film with ultrafine tin oxide nanoparticles smaller than 5 nm or single structure of SnO_2 (T) exhibited the good sensitivity (R_{3500}/R_{1000}) of 0.63 after aging at 400°C for 2 hours. The response time and recovery time of less than 0.4 and 1.6 minute was achieved.

In chapter 4, Pt catalyst was loaded instead of Pd in order to enhance the gas sensing properties better than those achieved values from Pd catalyst, because the achieved gas sensing properties in chapter 3 are not sufficient to satisfy the goal values of this thesis. The loading of Pt catalyst was also carried out at 300°C, and growth of nanoparticles was also successfully suppressed. As well, even after heat-treatment at 500°C for fabrication of gas sensitive thick film, the particle growth could be successfully suppressed. This is also attributed to the additive effects on interface migration. So, the gas sensitive thick film with Pt loaded tin oxide nanoparticles smaller than 5 nm and single structure of SnO_2 (T) exhibited the enhanced sensitivity (R_{3500}/R_{1000}) of 0.59 after aging at 400°C comparing with that of 0.63 using Pd catalyst. Also, recovery time was enhanced to less than 1.0 minute with same response time of 0.4 minute.

In chapter 5, for optimizing the gas sensing properties, optimization of catalytic configuration was attempted using Pd-Pt single and binary system with low temperature catalyst loading. As a result, gas sensing properties were changed with the Pd-Pt composition ratio, heat-treatment temperature, and operation temperature, and the catalytic configuration was optimized to 3 wt% single Pt catalytic system. It is owing to the dominant gas sensing mechanism, spillover or Fermi-level control, which is generated from the catalytic configuration such as metal or oxide form. The phenomena can be expressed as following equations of $\Delta H_{Pt} < \Delta H_{PdO}$ and $R_m = A \cdot \exp(-\Delta H_m/kT)$. From the equations, $R_{Pt} > R_{PdO}$, and it means that the reaction rate of Pt catalyst is higher than that of PdO catalyst, and Pt catalyst is considered to show superior behavior to PdO catalyst. Also, the optimized catalytic system showed the optimal gas sensing properties such as stable sensitivity of 0.58 with small deviation less than 3.5% and response and recovery time less than 0.4 and 1.0 minute. Therefore, high performance gas sensitive thick film could be fabricated by 3 wt% Pt single catalytic configuration.

In chapter 6, for high throughput, in-situ nanoparticle synthesis and catalyst loading method was developed. In-situ method is to synthesize the nanoparticle and load the catalyst simultaneously. In this case, the in-situ method could be succeeded by substituting SnO_2 nanoparticle to Sn acetate, which is perfectly dissolved into the solvent with catalyst materials such as Pd acetate and Pt acetylacetonate. The size of SnO_2-Pd nanoparticle synthesized by the in-situ method was less than 5 nm, and catalyst was uniformly distributed on the SnO_2 nanoparticle. Interestingly, contrary to the results in previous chapters, gas sensitive thick films with lower resistance showed better sensitivity. It is attributed to the oxygen vacancy that acts as electrical carriers in the nanoparticle synthesized by in-situ method. So, the sensitivity of the gas sensitive thick film fabricated by applying the in-situ SnO_2-Pd nanoparticle is superior to that of current SnO_2-Pd nanoparticle. The gas sensitive thick film composed of the SnO_2-3 wt% Pd nanoparticle exhibited good sensitivity of 0.58 after aging at 400°C for 5 hours. So, the SnO_2-Pd nanoparticle could be synthesized successfully by using the in-situ synthesis and loading method.

In chapter 7, for approaching to commercialization, long-term stability of gas sensing properties was investigated using the optimized gas sensitive thick films. As a result, shown in Fig. A-2, the gas sensitive thick film of 3 wt% Pt loaded SnO_2 nanoparticle made by inert gas condensation and low temperature catalyst loading exhibited the best stability of sensing properties of 0.58 after aging at 400°C for 1050 hours. Also, gas sensitive thick film of 3 wt% Pt or Pd loaded SnO_2 nanoparticle showed good response and recovery time of less than 0.4 and 1.0 minute smaller than those of Commercial (F company) sensor. Therefore, gas sensitive thick film with good long-term stability could be fabricated using the 3 wt% Pt loaded SnO_2 nanoparticle made by inert gas condensation and low temperature catalyst loading.

In chapter 8, as conclusions, physical properties of the SnO_2 nanoparticle synthesized by inert gas condensation could be optimized with 3 wt% Pt catalyst by developing and applying the low temperature catalyst loading method. The optimized physical properties led to enhanced sensing properties of gas sensitive thick film to CH_4 gas, and its long-term gas sensing properties was certified to be stable and suitable for commercialization.

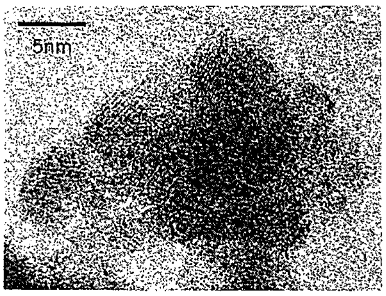
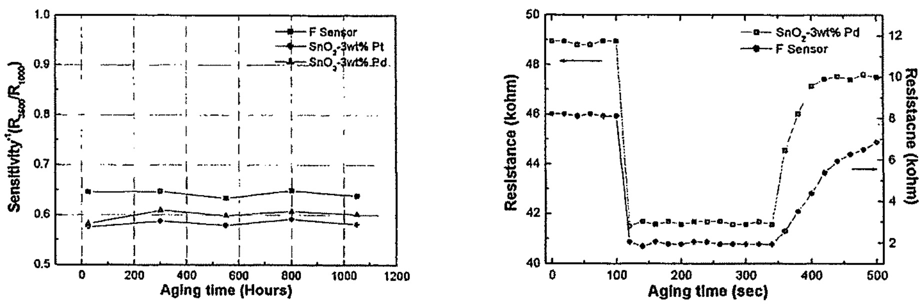


Fig. A-1. Catalyst loaded tin oxide nanoparticle by low temperature catalyst loading.



(a) Sensitivity (b) Response and recovery time

Fig. A-2. Enhancement of long-term stability of gas sensing properties.

論文審査結果の要旨

次世代のエネルギー源として燃料電池が注目されており、その原料ガスとしてメタンが使用されている。このため、事故防止のため高感度メタンガスセンサの開発が急務となっている。本研究は、酸化錫ナノ粒子をベースに、Pt あるいは Pd 触媒を付与し、ナノ粒子の粒成長を抑えるために低温プロセスを開発することによって、従来の市販品に比し応答速度および回復時間が優れたメタンガスセンサの開発に成功して経緯を纏めたもので、全8章よりなる。

第1章は緒論であり、本研究の背景と目的について述べている。

第2章は実験方法であり、本研究で用いた酸化錫ナノ粒子作製、触媒付与の方法、ガスセンサの作製法および評価手法について述べている。

第3章では、パラジウムアセテートを用いることにより、従来の塩化物を用いた方法に比べ、300度低い、300℃においてPd触媒の付与方法を確立すると共に、酸化錫ナノ粒子表面のPd粒子は酸化錫の粒成長を抑制することを明らかにした。

第4章では、白金アセチルアセトネートを用い、低温プロセスによる白金触媒を付与した酸化錫ナノ粒子ガスセンサーの作成を行い、3章で得られたPd触媒の結果と比較を行った。Ｐｄに比べ、Ptの方が優れた特性を有することを明らかにした。

第5章は、第3章および4章においてＰｔおよびＰｄのガス検出機構が異なることから、パラジウムアセテートおよび白金アセチルアセトネートＰｔおよびＰｄ触媒の同時付与のセンシング特性に与える影響を調べた。

第6章は、Sn アセテートと白金アセチルアセトネートの溶液から、Pt触媒を付与した酸化錫ナノ粒子の同時合成法を開発した。

第7章は、センサ特性の長時間安定性の評価を行い、実用化に必要な安定性を示すことを明らかにした。

第8章は結論で、本研究で得られた成果を総括している。

以上要するに、本研究は、Pd 触媒を付与した酸化錫ナノ粒子を用いたメタンガスセンサ作製のための低温プロセスを開発し、従来の市販品に比べ極めて優れた特性を有するメタンガスセンサの開発に成功したもので、材料工学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。